I. THE DIELS-ALDER REACTION WITH UNSATURATED ANILS

II. THE PREPARATION OF ALKYLBORON DIFLUORIDES

BY
JOHN CUTLER ROBINSON, JR.
B.S., Boston University, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PART I. THE DIELS-ALDER REACTION WITH UNSATURATED ANILS

Introduction

One example of a true Diels-Alder reaction of an unsaturated Schiff base has been reported; in the presence of maleic anhydride, 2-ethyl-2-hexenalaniline reacts in its tautomeric dieneamine form to yield 5,7-diethyl-2-phenyl-2-azabicyclo-(2, 3,1)-oct-6-ene-3-one-8-carboxylic acid.[1] Since the reaction is irreversible under the conditions employed, it should be possible to use it in testing for the presence of the anil as a component of an equilibrium mixture. A second object of the present study was the investigation of the scope of the condensation, particularly with reference to the effect of the substituent on the nitrogen atom.

Discussion

Maleanilic acid has been found to react with 2-ethyl-2-hexenal and 2-methyl-2-pentenal to yield bicyclic amido acids identical with those obtained from maleic anhydride and the anils of the unsaturated aldehydes. The occurrence of this reaction is considered as evidence for the reversibility, at moderate temperatures, of the reaction between acid anhydrides and anils. This method of preparing the condensation products is more convenient than that[1] formerly employed.

When N-(*p*-bromphenyl)- and N-(*p*-tolyl) maleamic acids were substituted for maleanilic acid, the bicyclic amido acids containing the corresponding *p*-substituted phenyl groups were obtained. Experiments designed to produce adducts containing methyl, butyl and heptyl substituents on the nitrogen atom yielded only non-crystalline, viscous oils. Attempts to prepare the bicyclic molecules carrying hydroxyl, methoxyl and dinitroaniline groups on the 2 position failed. The basic strength of the amine used appeared to have no effect upon those reactions from which characterizable products were obtained.

Although aldehyde-ammonias or imines from α,β-unsaturated aldehydes have not been reported, evidence that such imines may exist has been obtained. Maleamic acid (maleic acid monoamide) was condensed with 2-ethyl-2-hexenal to give a bicyclic amido acid identical in ring structure with those prepared from the maleanilic acids. By analogy with the former reactions, this process probably proceeds by the formation of maleic anhydride and the imine from the aldehyde, these compounds then condensing to give the Diels-Alder adduct.

The mechanism proposed for the formation of Diels-Alder adducts from aldehydes and maleamic acids assumes the initial addition of the amide function of the maleamic acid to the aldehyde. This intermediate then may lose maleic acid to give the imine or substituted imine. The maleic acid is in equilibrium with its anhydride under the conditions of the reaction and the unsaturated imine is in equilibrium with the tautomeric dieneamine. The anhydride and the dieneamine combine as previously described.[1]

Attempts to prepare derivatives of the dieneamine form of 2-ethyl-2-hexenalaniline other than Diels-Alder adducts and to obtain degradation products of this tautomer failed.

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PART II. THE PREPARATION OF ALKYLBORON DIFLUORIDES

Introduction

It has been shown recently that the trialkylborines are effective to varying degrees as catalysts for the polymerization of certain vinyl-type monomers.[1] Alkylboron difluorides, which may be considered as derivatives of boron trifluoride with one of the fluorine atoms replaced by an alkyl group, might be expected to possess catalytic activity intermediate between that of boron trifluoride and those of the borines. Presumably, catalysts of a wide range of activity might be prepared by the proper choice of the alkyl group in the alkylboron difluoride. Accordingly, an investigation of the methods of

synthesis of compounds of this type was undertaken with a view to making them available for study as polymerization catalysts.

Discussion

Two methods have been reported for the preparation of organoboron fluorides. Phenylboron diflouride is said to be formed from boron trifluoride in absolute ether and phenylmagnesium bromide.[2] In attempts to use this procedure in the preparation of phenyl- and heptylboron difluorides, only small amounts of impure products were obtained. In attempts to prepare methylboron difluoride in this manner, only trimethylborine was obtained.

The second reported method consists in the treatment of methaneboronic anhydride with boron trifluoride to produce methylboron difluoride.[3] Apparently, the reaction has been carried out under very mild conditions. When boron trifluoride was bubbled through heptaneboronic anhydride at temperatures ranging from 25° to 200°, the unchanged anhydride was recovered. The treatment of ethaneboronic anhydride with boron trifluoride under a pressure of 1000 pounds per square inch produced ethylboron difluoride, a fuming liquid boiling at —24°. This modification of the method may permit the synthesis of other alkylboron fluorides from less active anhydrides.

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VITA

The writer was born in Reading, Massachusetts, on January 18, 1918. He attended the public schools of that town and graduated from Reading High School in June, 1934. In September, 1935, after a post-graduate year in high school, he entered Boston University, from which he received the Degree of Bachelor of Science in June, 1939. Since September of that year, he has been studying for the Degree of Doctor of Philosophy in the Graduate School of the University of Illinois. From September, 1940, to June, 1942, he held a Special Research Assistantship and, from September, 1942 to June, 1943, he has held a University Fellowship.

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